



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G02B 6/44</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/18493</b> <b>(43) International Publication Date:</b> 22 May 1997 (22.05.97)
<b>(21) International Application Number:</b> PCT/US96/17800 <b>(22) International Filing Date:</b> 7 November 1996 (07.11.96)  <b>(30) Priority Data:</b> 558,125 13 November 1995 (13.11.95) US  <b>(71) Applicant:</b> LIGHTGUIDE MATERIALS, INC. [US/US]; 1500 Wilson Way, Smyrna, GA 30082 (US).  <b>(72) Inventor:</b> LEVY, Alvin, C.; 1056 Winding Branch Court, Dunwoody, GA 30338 (US).  <b>(74) Agent:</b> PABST, Patrea, L.; Arnall Golden & Gregory L.L.P., 2800 One Atlantic Center, 1201 West Peachtree Street, Atlanta, GE 30309-3450 (US).		<b>(81) Designated States:</b> AU, CA, CN, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MATRIX COMPOUNDS FOR FORMING OPTICAL FIBER RIBBONS  <b>(57) Abstract</b>  A removable matrix for retaining one or more optical fibers which have an outermost layer made of a first polymer having a first initiator system, e.g., a free-radical initiated, ultraviolet curable acrylate polymer, where the matrix is made from a second polymer having a second initiator system substantially different from the first initiator system, e.g., a cationically initiated, ultraviolet curable vinyl ether polymer. An optical fiber and matrix ribbon, where the ribbon is made from optical fibers which have an outermost layer of a free-radical initiated, ultraviolet radiation curable acrylate polymer, and a removable matrix for retaining the optical fibers, wherein the matrix comprises a cationically initiated, ultraviolet radiation curable polymer. An optical fiber and matrix ribbon which is made from optical fibers having an outermost layer made of a cationically initiated, ultraviolet radiation curable polymer, and a removable matrix for retaining the optical fibers, where the matrix is made from a free-radical initiated, ultraviolet radiation curable acrylate polymer. An ink for use on an acrylate polymer coated optical fiber, wherein the ink contains an inhibitor of cationically initiated polymerization. A matrix comprised of a cationically initiated, ultraviolet radiation curable vinyl ether polymer.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## MATRIX COMPOUNDS FOR FORMING OPTICAL FIBER RIBBONS

### Background of the Invention

5     Field of the Invention:

The invention relates to optical fibers. In particular, the present invention relates to novel ribbon systems composed of optical fibers and a removable matrix wherein the polymer systems of the optical fibers and the removable matrix use different initiator systems.

10    Background Art:

In the typical ribbon design for optical fiber (glass) cables, a number of coated optical fibers or color-coded, coated optical fibers are first arranged in a flat array. The fiber coating is generally an ultraviolet (UV) curable acrylate and the optional color-coding material is either a  
15    solvent based vinyl ink or a UV curable acrylate based ink. The fiber array is then overcoated with a thin layer of what is referred to as a "matrix coating," which is then cured. The purpose of the cured material is to provide integrity to the ribbon structure. The most common matrix materials are UV curable acrylates and such matrix materials are present  
20    in, *e.g.*, the AT&T Accuribbon®. The AT&T Accuribbon® product literature shows a matrix material having a thickness of as little as 0.03 mm at the top of the fiber up to as great as 0.125 mm in the valleys between adjacent fibers.

There is not common agreement in the industry as to the specific  
25    mechanical properties the matrix compound must have to be functional over the wide temperature ranges the cable might experience, from about -40°C to approximately 80°C. Both low modulus materials, less than 100 MPa, and high modulus materials, above 900 MPa, are presently employed by various cable manufacturers. However, it is generally  
30    accepted that the compound must be stable at conditions of high

-2-

temperature and high relative humidity for some cable design applications. For example, Bellcore Technical Reference TR-NWT-000020 requires testing some cable components at 85°C and 85% relative humidity for 30 days. Additionally, it must be possible to easily remove the coated  
5 optical fibers or color coded, coated optical fibers from the ribbon without damaging the coated fibers or removing the color coding where a color code is present. The latter requirement is important for fiber splicing and connectorization.

In another prior art ribbon, a layer of pressure sensitive tape on  
10 each side of the fiber array was used to form the ribbon. This construction provided for easy fiber removal. However, because of high signal attenuation and high costs associated with this design, the industry has now switched to UV curable acrylates to bond the fiber array, as opposed to the pressure sensitive tape. This change has led to difficulties  
15 in fiber breakout (separation) from the ribbon without damaging the fiber. For instance, in the case of the AT&T Accuribbon®, the ribbon must first be treated with an alcohol-based gel to swell the matrix coating sufficiently to accomplish fiber removal in the required manner.

An alternate prior art ribbon design, which avoids the need for the  
20 chemical treatment experienced with the Accuribbon®, is disclosed in U.S. Patent 4,828,349. In the '349 disclosure, a peel layer is placed around the outside of the optical fiber and then a covering layer (matrix layer) is overlayed to form the ribbon structure. The peel layer is comprised of a thermosetting or ultra violet curable fluorocarbon or  
25 silicone resin. Because of the presence of the peel layer, the matrix or covering layer can be easily removed without damaging the peel layer.

Cationic and free-radical based polymerization is discussed generally in Rudin, A., *The Elements of Polymer Science and Engineering*, Academic Press, Inc., NY (1982).

30 For these reasons, it is highly desirable to provide a ribbon having a readily removable matrix while overcoming the disadvantages of the

-3-

prior art, such as not needing a gel treatment or a special application of a peel layer, to facilitate easy removal of the fibers from the ribbon.

### SUMMARY OF THE INVENTION

The present invention provides a system which overcomes the  
5 prior art disadvantages because the present invention, for example, does  
not require gel treatment or a special peel layer to permit easy removal of  
the fibers from the ribbon. In particular, the present invention provides a  
removable matrix for retaining one or more optical fibers having an  
outermost layer comprising a first polymer with a first initiator system,  
10 the matrix comprising a second polymer having a second initiator system  
substantially different from the first initiator system.

In addition, the present invention provides an optical fiber and  
matrix ribbon, the ribbon comprising one or more optical fibers, wherein  
the fibers have an outermost layer comprising a free-radical initiated,  
15 ultraviolet radiation curable acrylate polymer, and a removable matrix for  
retaining the one or more optical fibers, wherein the matrix comprises a  
cationically initiated, ultraviolet radiation curable polymer.

In yet another embodiment, the present invention provides an ink  
for use on an acrylate polymer coated optical fiber, wherein the ink  
20 comprises an inhibitor of cationically initiated polymerization.

Furthermore, the present invention provides a matrix comprised of  
a cationically initiated, ultraviolet radiation curable vinyl ether polymer.

Additional advantages of the invention will be set forth in part in  
the description which follows, and in part will be obvious from the  
25 description, or may be learned by practice of the invention. The  
advantages of the invention will be realized and attained by means of the  
elements and combinations particularly pointed out in the appended  
claims. It is to be understood that both the foregoing general description  
and the following detailed description are exemplary and explanatory only  
30 and are not restrictive of the invention, as claimed.

### Detailed Description of the Preferred Embodiments

The present invention may be understood more readily by reference to the following detailed description of preferred embodiments of the invention.

5        Before the present devices and methods are disclosed and described, it is to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. It must be noted that, as used in the specification and the appended claims, the singular forms "a", "an" and "the" include plural  
10        referents unless the context clearly dictates otherwise.

As used herein, the term "removable" means that the matrix and the optical fiber may be separated or peeled apart without damaging the outermost layer of the optical fiber. Also, as used herein, the "outermost layer" of the optical fiber may either be the actual outer polymer coating  
15        of the fiber or, when present, the coating layer formed by any ink applied to the optical fiber, whichever is outermost. Furthermore, as used herein, the term "initiator system" is used to describe the various polymerization initiation reactions, including, but not limited to, cationic initiator systems, anionic initiator systems and free-radical initiator systems. As  
20        used herein, the term "radiation" is applied to a cure system for polymers which requires the input of energy, *e.g.*, heat, microwave, or ultraviolet radiation. Therefore, a "radiation curable" polymer is one which can be cured by the application of radiation and an "ultraviolet radiation curable polymer" is one which is cured by the application of ultraviolet radiation.  
25        In addition, the term "ribbon" is used herein to refer to an article resulting from one or more optical fibers, with or without an ink coating, coated with a matrix compound. While the "ribbon" is generally described as a flat cable of multiple optical fibers, such limitation is not necessary and shall not be construed as a limitation on the present  
30        invention.

In addition, as used herein, "substantially different" initiator systems means that the initiator systems of the major portions of the

-5-

specified polymers are different. For instance, a polymer having a major portion of a free-radical initiated acrylate and a minor portion of a cationically initiated polyol would have a substantially different initiator system from a polymer having a major portion of a cationically initiated polyol, cycloaliphatic epoxide or vinyl ether and a minor portion of a free-radical initiated acrylate polymer.

The present invention provides a removable matrix for retaining one or more optical fibers having an outermost layer comprising a first polymer with a first initiator system, the matrix comprising a second polymer having a second initiator system substantially different from the first initiator system. In a further embodiment, the first and second polymers are radiation curable polymers. In yet a further embodiment, the first polymer comprises a free radical initiated, ultraviolet radiation curable polymer and the second polymer comprises a cationically initiated, ultraviolet radiation curable polymer.

The present invention also discloses the matrix wherein the free radical initiated, ultraviolet radiation curable first polymer is an acrylate polymer. In a further embodiment, the matrix second polymer further comprises a partial adhesion promoting amount of a free-radical initiated, radiation curable acrylate polymer and wherein the cationically initiated, ultraviolet radiation curable polymer comprises a major portion of the matrix and the free-radical initiated, ultraviolet radiation curable acrylate polymer comprises a minor portion of the matrix, whereby the presence of the free-radical initiated, ultraviolet radiation curable acrylate polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

In yet another embodiment, the cationically initiated, ultraviolet radiation curable second polymer comprises a mixture of cycloaliphatic epoxide and a polyol. In a further embodiment, the cationically initiated, ultraviolet radiation curable second polymer comprises a vinyl ether polymer. In a further embodiment, the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer,

-6-

a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof. Specifically, the vinyl ether encapped ester oligomer is Allied Signal 150B, the vinyl ether encapped urethane oligomer is Vectomer 2032, the vinyl ether encapped monomer is bis-(4-  
5 vinyloxybutyl) isophthalate and the vinyl ether encapped monomer is 4-vinyloxybutyl benzoate.

In a further embodiment of the invention, the first polymer comprises a cationically initiated, ultraviolet radiation curable polymer and the second polymer comprises a free radical initiated, ultraviolet  
10 radiation curable polymer. In yet another embodiment, the free radical initiated, ultraviolet radiation curable polymer is an acrylate polymer. In another embodiment, the matrix further comprises a partial adhesion promoting amount of a cationically initiated, ultraviolet radiation curable polymer and wherein the free-radical initiated ultraviolet radiation curable  
15 polymer comprises a major portion of the matrix and the cationically initiated, ultraviolet radiation curable polymer comprises a minor portion of the matrix, whereby the presence of the cationically initiated, ultraviolet radiation curable polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

20 In addition, the present invention provides an optical fiber and matrix ribbon, the ribbon comprising one or more optical fibers, wherein the fibers have an outermost layer comprising a free-radical initiated, ultraviolet radiation curable acrylate polymer, and a removable matrix for retaining the one or more optical fibers, wherein the matrix comprises a  
25 cationically initiated, ultraviolet radiation curable polymer. In a further embodiment, the matrix further comprises a free-radical initiated, radiation curable acrylate polymer and wherein the cationically initiated, ultraviolet radiation curable polymer comprises a major portion of the matrix and the free-radical initiated, ultraviolet radiation curable acrylate  
30 polymer comprises a minor portion of the matrix, whereby the presence of the free-radical initiated, ultraviolet radiation curable acrylate polymer promotes partial adhesion between the outermost layer of the one or more



-7-

fibers and the matrix. In yet another embodiment, the cationically initiated, ultraviolet radiation curable polymer comprises a vinyl ether polymer. In a further embodiment, the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer, 5 a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof. Specifically, the vinyl ether encapped ester oligomer is Allied Signal 150B, the vinyl ether encapped urethane oligomer is Vectomer 2032, the vinyl ether encapped monomer is bis-(4-vinyloxybutyl) isophthalate and the vinyl ether encapped monomer is 4-10 vinyloxybutyl benzoate.

In addition, the present invention provides a ribbon wherein the outermost layer of the one or more fibers comprises an ink coating, wherein the ink comprises a free-radical initiated, radiation curable acrylate polymer. In a further embodiment, the ink further comprises an 15 inhibitor of cationically initiated polymerization. In yet another embodiment, the inhibitor is water, a basic compound, or a mixture thereof. More specifically, the inhibitor is a pigment capable of interacting with the cation, or a hindered amine light stabilizer, such as bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate, or the inhibitor is 1-vinyl-2-20 pyrrolidone.

In yet another embodiment of the ribbon, the ribbon comprises one or more optical fibers, wherein the fibers have an outermost layer comprising a cationically initiated, ultraviolet radiation curable polymer, and a removable matrix for retaining the one or more optical fibers, 25 wherein the matrix comprises a free-radical initiated, ultraviolet radiation curable acrylate polymer. In a further embodiment, the matrix further comprises a cationically initiated, ultraviolet radiation curable polymer and wherein the free-radical initiated, ultraviolet radiation curable acrylate polymer comprises the major portion of the matrix and the cationically 30 initiated, ultraviolet radiation curable polymer comprises the minor portion of the matrix, whereby the presence of the cationically initiated, ultraviolet radiation curable polymer promotes partial adhesion between

the outermost layer of the one or more fibers and the matrix. In yet another embodiment, the cationically initiated, ultraviolet radiation curable polymer comprises a vinyl ether polymer. Moreover, in an alternate embodiment, the outermost layer of the one or more fibers comprises an ink coating, wherein the ink comprises a cationically initiated, ultraviolet radiation curable polymer. In an alternate embodiment, the ink further comprises an inhibitor of free-radical initiated polymerization. In another embodiment, the inhibitor comprises a benzoquinone derivative, such as hydroquinone, naphthaquinone, or a mixture thereof.

In yet another embodiment, the present invention provides an ink for use on an acrylate polymer coated optical fiber, wherein the ink comprises an inhibitor of cationically initiated polymerization. In an alternate embodiment, the inhibitor is water, a basic compound, or a mixture thereof. In yet another embodiment, the inhibitor is a pigment capable of interacting with the cation. In yet another embodiment, the basic compound comprises a hindered amine light stabilizer, such as bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate. In an alternate embodiment, the inhibitor is 1-vinyl-2-pyrrolidone. In another alternate embodiment, the inhibitor is an initiator of free radical initiated polymerization, such as 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1.

The present invention also provides a matrix comprised of a cationically initiated, ultraviolet radiation curable vinyl ether polymer. In a further embodiment, the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer, a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof. Specifically, the vinyl ether encapped ester oligomer is Allied Signal 150B, the vinyl ether encapped urethane oligomer is Vectomer 2032, the vinyl ether encapped monomer is bis-(4-vinyloxybutyl) isophthalate and the vinyl ether encapped monomer is 4-vinyloxybutyl benzoate.

The present invention involves the selection and formulation of the matrix material or both the matrix material and the ink such that an

optical fiber cable manufacturer may choose the level of adhesion between the coated or the color-coded, coated optical fibers and the matrix coating used in the fiber ribbon. Using the methods of the present invention, neither a gel treatment nor a special application of a peel layer is required to facilitate easy removal of the fibers from the ribbon.

Most optical fibers in use in the industry today use an outer coating composed of free-radical initiated, UV curable acrylate polymers. For such optical fibers, the present invention proposes the use of a cationically initiated, UV curable material as the major portion of the matrix coating formulation. The use of polymers having distinct initiator systems prevents extensive cross-linking or other binding between the outermost layer of the optical fiber and the matrix. Moreover, the matrix coating may also contain free-radical initiated, UV curable acrylates to properly balance the adhesion, *i.e.*, to increase the adhesion to the ink or fiber coating to a desired level. Additionally, the use of some acrylate materials reduces the raw material cost of the completed matrix compound because acrylate materials are presently less expensive than cationically initiated materials.

Moreover, in embodiments where acrylate polymers are used to increase the partial adhesion, the use of high molecular weight acrylates and the functionality of the acrylate may be manipulated to increase or decrease adhesion. For instance, a higher molecular weight acrylate would provide for less adhesion because the functional equivalent weight (*i.e.*, weight divided by degree of functionality) would be higher. The degree of functionality of the acrylate polymer used can also be chosen to increase or reduce the adhesion, where an increase in the degree of functionality would increase the adhesion.

Additionally, formulation latitude is further increased if the ink (which forms the outermost layer of the optical fiber) used to optionally color-code the fiber contains a component which slightly inhibits the cure of the matrix compound at the interface between the matrix compound and the ink. The degree of inhibition of cure influences the level of adhesion

-10-

at the interface and hence the relative ease of removing the fiber from the matrix coating.

The ink used to color-code the fiber can have many different chemistries with the exception that, for systems using a cationically initiated, UV curable polymer in the matrix, the major components cannot be cationically initiated UV curable materials. Examples of commonly used inks are solvent based vinyl inks and free-radical initiated, UV curable acrylate inks.

Generally, cationically initiated materials are inhibited by molecules which can hydrogen bond or react with the cation and therefore remove it from its role in the reaction. Examples of inhibitors include, but are not limited to, water, bases (even very weak bases present in the fiber coating, such as hindered amine light stabilizers), other components often present in UV curable acrylates such as N vinyl pyrrolidone (1-vinyl-2-pyrrolidone), and even selected pigments capable of interacting with the cation. The degree of inhibition can vary widely by component and with concentration.

For the case where the outer coating on the optical fiber (as opposed to the matrix) is a cationically initiated UV curable vinyl ether material (*see, e.g.*, U.S. Patent No. 5,139,872), the ink can be comprised substantially of cationically initiated UV materials where a UV ink is used. The matrix compound in this case is comprised substantially of free radical initiated, UV curable acrylate components. The important distinction is that while the ink, if used, and optical fiber outer coating share the same initiator system, the matrix polymer must use a distinct or different initiator system than the outermost layer, either the ink, if used, or the outer polymer coating of the optical fiber. Similar to the cationic cure matrix instance, inhibition of cure can be controlled by including a low level of a free-radical scavenger in the ink or the fiber coating where the color coding inks are not used. For instance, a benzoquinone derived free-radical scavenger such as hydroquinone or naphthaquinone can be added to the ink.

Preferred matrix material formulations useful for the present invention are given in Tables 1 and 2. Table 1 details formulations where the reactive components are based on vinyl ether chemistry. Table 2 contains formulations based on cycloaliphatic epoxides and polyols chemistry and mixed systems of the two chemistries.

In Table 1, Allied Signal 150B (Allied Signal, Inc., Morristown, NJ) is a vinyl ether encapped polyester oligomer having a viscosity of 340,000 cps at 60°C and a weight average molecular weight of from 2000 to 3500. Vectomer 2032 (Allied Signal, Inc., Morristown, NJ) is a vinyl ether encapped urethane oligomer which has a viscosity of 30,000 cps at 70°C and a weight average molecular weight of 4800 to 6600. Bis-(4-vinyloxybutyl) isophthalate is a difunctional (with respect to cationic cure) vinyl ether monomer with a viscosity of 85 cps at 25°C and is sold under the trade name Vectomer 4010 (Allied Signal, Inc., Morristown, NJ). 4-vinyloxybutyl benzoate is a monofunctional vinyl ether monomer (with respect to cationic cure) having a viscosity of 7 cps at 25°C and is available under the trade name Vectomer 3010 (Allied Signal, Inc., Morristown, NJ).

Other preferred vinyl ether compounds that are particularly suitable for the matrix compositions of the present invention include, but are not limited to, 1,4-bis[(vinyloxy)methyl]-cyclohexane (1,4-cyclohexanedimethanol divinyl ether), sold under the trade name Rapi-Cure CHVE (International Specialty Products, Inc., Wayne N.J.) and having a viscosity of 5.0 cps at 25°C; 3,6,9,12-tetraoxatetradeca-1,13-diene (triethylenc glycol divinyl ether), sold under the trade name Rapi-Cure DVE-3 (International Specialty Products, Inc., Wayne, N.J.) and having a viscosity of 2.67 cps at 25°C; hydroxybutyl vinyl ether, sold under the trade name Rapi-Cure HBVE (International Specialty Products, Inc., Wayne, N.J.) and having a viscosity of 7.5 cps at 25°C; n-dodecyl vinyl ether, sold under the trade name Rapi-Cure DDVE (International Specialty Products, Inc., Wayne, N.J.) and having a viscosity of 2.81 cps at 25°C; bis-(4-vinyloxymethylcyclohexyl methyl) glutarate, sold under

-12-

the trade name Vectomer 4020 (Allied Signal Corp., Morristown, N.J.) and having a viscosity of 430 cps at 25°C; and bis-(4-vinyloxybutyl) succinate (International Specialty Products, Inc., Wayne, N.J.) having a viscosity of 43 cps at 25°C. Other suitable vinyl ethers include, but are not limited to, ethyl vinyl ether, propyl vinyl ether, isobutyl vinyl ether, octadecyl vinyl ether, butyl vinyl ether, ethyleneglycol vinyl ether, diethyleneglycol divinyl ether, butanediol monovinyl ether, butanediol divinyl ether, ethyleneglycol butyl vinyl ether, triethyleneglycol methyl vinyl ether, cyclohexanedimethanol monovinyl ether, 2-ethylhexyl vinyl ether, Poly-THF-divinyl ether 290, pluriol-E-200-divinyl ether, cyclohexyl vinyl ether, tert-butyl vinyl ether, tert-amyl vinyl ether, ethyleneglycol divinyl ether, diethyleneglycol monovinyl ether, hexanediol monovinyl ether, tetraethyleneglycol divinyl ether, trimethylolpropane trivinyl ether, aminopropyl vinyl ether, or 2-diethylaminoethyl vinyl ether (preceding vinyl ethers available from BASF, Mount Olive, N.J.).

In addition, there are many acrylate polymers ("acrylates") in use today which are suitable for the purposes described herein. More particularly, for the purposes of the examples discussed herein, Ebecryl 8804 is the trade name for an aliphatic urethane acrylate oligomer with a viscosity of 10,000 - 24,000 cps at 65°C, a molecular weight of 1,400 and a functionality of 2.4 (UCB Radcure Inc., Smyrna, GA). Tripropylene glycol diacrylate (TRPGDA) is a difunctional monomer with a viscosity of 12 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Trimethylopropane triacrylate (TMPTA) is a trifunctional monomer with a viscosity of 85 cps at 25°C (UCB Radcure Inc., Smyrna, GA). 1,6-hexanediol diacrylate (HDODA) is a difunctional monomer with a viscosity of 6 cps at 25°C (UCB Radcure Inc., Smyrna, GA).  $\beta$ -carboxyethyl acrylate ( $\beta$ -CEA) is a monofunctional monomer with a viscosity of 75 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Isobornyl acrylate (IBOA) is a monofunctional monomer with a viscosity of 9.5 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Octyl/decyl acrylate (ODA) is a monofunctional monomer with a viscosity of 2 cps at 25°C (UCB

-13-

Radcure Inc., Smyrna, GA). Oxyethylated phenol acrylate (Ebecryl® 110) is a monofunctional monomer with a viscosity of 75 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Tetraethylene glycol diacrylate (TTEGDA) is a difunctional monomer with a viscosity of 20 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Bisphenol-A derivative diacrylate (Ebecryl® 150) is a difunctional monomer with a viscosity of 1,500 cps at 25°C (UCB Radcure Inc., Smyrna, GA). OTA-480 is a trifunctional monomer with a viscosity of 85 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Pentaerythritol triacrylate (PETA-K) is a trifunctional monomer with a viscosity of 500 cps at 25°C (UCB Radcure Inc., Smyrna, GA). PETA-LQ is a lower functionality version of PETA-K with a viscosity of 1,500 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Trimethylolpropane ethoxy triacrylate (TMPEOTA) is a trifunctional monomer with a viscosity of 20 cps at 25°C (UCB Radcure Inc., Smyrna, GA). Acrylated di-pentaerythritol (DPHPA) is a multifunctional monomer with a viscosity of 20,000 cps at 25°C (UCB Radcure Inc., Smyrna, GA). In addition, other Ebecryl® acrylates suitable for the present purposes include, but are not limited to, Ebecryl® 80, 81, 82, 220, 230, 244, 264, 265, 270, 284, 285, 436, 438, 450, 505, 524, 525, 584, 585, 586, 588, 600, 605, 616, 629, 639, 657, 745, 754, 767, 770, 810, 830, 860, 870, 1290, 1608, 1657, 1701, 1755, 1810, 3200, 3201, 3409, 3500, 3502, 3600, 3603, 3604, 3605, 3608, 3700, 3700-20H, 3700-20T, 3700-25R, 3701, 3701-20T, 3702, 3703, 4827, 4830, 4833, 4834, 4849, 4866, 4881, 4883, 6602, 6700, 8301, 8402, 8800, 8800-20R, or 8803 (All Ebecryl® product numbers available from UCB Radcure Inc., Smyrna, GA).

Ar<sub>3</sub>SPF<sub>6</sub> in the presence of UV light can serve as the initiator in the cationic polymerization of vinyl ether oligomers and monomers and is sold under the trade name UVI 6990 (Union Carbide, Danbury, CT). 2,2-dimethoxy-2-phenylacetophenone is a Norish Type 1 Cleavage photo initiator with a melting point of 63-66°C and is available sold under the trade name Irgacure 651 (Ciba-Geigy Corp., Hawthorne, NY). Irgacure

-14-

651 serves as the free radical source on exposure to UV light for the polymerization of acrylate monomers and oligomers. Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate is a thermal oxidative stabilizer which is available under the trade name Irganox 1076 (Ciba-Geigy Corp., Hawthorne, NY). The propenyl ether of propylene carbonate (RAPI-CURE PEPC) has a molecular weight of 158 and a viscosity of 13 cps at 25°C (International Specialty Products, Wayne, NJ or Charlotte, NC). PEPC helps to solubilize the UV 6990.

SF 1188 is the trade name for the copolymer of a polymethyl siloxane and a polyoxy alkene ether having a viscosity of 600-1200 cps at 25° C, a density of 1.04 g/cc avg., and a surface tension of 25.5 dynes/cm<sup>2</sup> (GE Silicones, Waterford, NY). SF 1188 is an anti-blocking agent which prevents tacking together of adjacent layers of ink or matrix when the product is wound upon itself.

In Table 2, UVR-6110 is the trade name for 3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate which has an epoxy equivalent weight of 131 - 143 and a viscosity at 25°C of 350 - 450 cps (Union Carbide, Danbury, CT.). See Carroy, Antoine, *Aspects of Photoinitiation: Cationic UV-Curing Efficiency of Cycloaliphatic Epoxide-Based Systems Through Photoinitiator and UV-Wavelength Selection* (1993). UVR-6128 is the trade name for bis-(3,4-epoxycyclohexyl) adipate which has an epoxide equivalent weight of 350-450 and a viscosity at 25°C 190 - 210 cps (Union Carbide, Danbury, CT.). Tone 0301 is the trade name for an  $\epsilon$ -caprolactone triol which has an hydroxyl equivalent weight of 98 - 103 and a viscosity of 2250 cps at 55°C (Union Carbide, Danbury, CT.). Tone 0301 is trifunctional with respect to reactivity. Tone 0201 is the trade name for a caprolactone diol having an average molecular weight of 530 and a viscosity of 65 cps at 55°C (Union Carbide, Danbury, CT.). Tone 0201 is difunctional with respect to reactivity.

Various other components at low addition levels such as wetting and anti-blocking agents and other components known in the art, such as



-16-

TABLE 1 - MATRIX FORMULATIONS:  
FORMULATION IDENTIFICATION (PARTS BY WEIGHT )

COMPONENTS:	1A	1B	1C	1D	1E	1F	1G	1H	1I	1J	1K	1L	1M	1N
<u>VINYL ETHERS:</u>														
ALLIED 150B	63.7		57.3	57.3	57.3	51	51	51	31.9	31.9	31.9		31.9	64
VECTOMER 2032		65.7												
VECTOMER 4010	21.2	20	19.1	19.1	19.1	17	17	17	10.6	10.6	10.6		10.6	21
VECTOMER 3010	10.6	10	9.5	9.5	9.5	8.5	8.5	8.5	5.3	5.3	5.3		5.3	15
<u>ACRYLATES:</u>														
EBERCRYL 8804												65	32.5	
TRPGDA				10			20				50	7	3.5	
TMPTA			10			20				50		18	9.0	
HDODA			10		20				50			10	5.0	
<u>ADDITIVES:</u>														
IRGANOX 1076	1.1	1.1	1.0	1.0	1.0	0.9	0.9	0.9	0.6	0.6	0.6	1.0	1.1	1.0
UVI 6990	1.3	1.3	1.2	1.2	1.2	1.0	1.0	1.0	1.2	1.2	1.2		1.2	1.2
IRGACURE 651			2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	2.0	
PEPC	2.1	2.0	1.9	1.9	1.9	1.7	1.7	1.7	1.1	1.1	1.1		1.1	2.0
SF1188												0.5	0.25	
<u>PROPERTIES:</u>														
Modulus (MPa):	731	400				710	986	497						490
Elongation @ Break (%)	37	38				21	9	36						52
Break Strength (MPa)	23.4	20.7				23.4	35.2	17.2						12.9
Modulus Change (%)														
(95C/95RH 20 DAYS)	+8.3	0				+24	+13	+24						
(95C/95RH 30 DAYS)	-7.5	+56				+36	+45	+37						
Viscosity 25 C (Poise)	208	370				11	21	45						98

-17-

**TABLE 2**  
**MATRIX FORMULATIONS**

COMPONENTS:	FORMULATION IDENTIFICATION (PARTS BY WEIGHT)					
	2A	2B	2C	2D	2E	2F
<u>CYCLOALIPHATIC EPOXIDES:</u>						
UVR 6110	75	60	75	65		60
UVR 6128					75	
<u>POLYOLS:</u>						
TONE 0201			25	35	25	20
TONE 0301	25	20				
<u>VINYL ETHERS:</u>						
ALLIED 150B						13.5
VECTOMER 4010						4.5
VECTOMER 3010						2.0
<u>ACRYLATES:</u>						
TRPGDA		20				
<u>ADDITIVES:</u>						
IRGANOX 1076	1.0	1.0	1.0	1.0	1.0	1.0
UVI 6990	4.0	4.0	4.0	4.0	4.0	3.0
IRGACURE 651		1.0				
SF 1188						
<u>PROPERTIES:</u>						
MODULES (MPa):	1117		703	200	103	579
ELONGATION MAX(%):	5.3		7.0	75	36	27
BREAK STRENGTH (MPa):	37.2		25.5	14.5	3.4	15.2
MODULUS CHANGE, (%), 95C/95RH 6 DAYS)			-76			
VISCOSITY 25 C (Poise)	3.9		3.0	2.6	3.8	

-18-

5           The 95°C/95% relative humidity (RH) conditioning was done in a  
Blue M Power-O-Matic 60 (Blue M Electric, Blue Island, IL)  
temperature/humidity oven. Samples were conditioned for at least 24  
hours at ambient after removal from the oven before testing. Viscosity  
was determined using either a Brookfield model LVF or a model RVT  
10 (Brookfield Engineering Laboratory, Inc., Stoughton, MA) viscometer.

Tensile data show a range of values from about 100 to 1000 MPa.  
The data show the usual variation in properties with crosslink density and  
the backbone flexibility. The effect of crosslink density is illustrated in  
Table 1 where use of the monofunctional monomer Vectomer 3010 in  
15 place of the difunctional monomer Vectomer 4010 (Formulations 1A and  
1N) leads to decrease in modulus associated with the decrease in crosslink  
density. The same can be seen in Table 2 where difunctional Tone 0201  
is used in place of the trifunctional Tone 0301 (Formulations 2A and 2C).  
The example of backbone flexibility can be seen in Table 2 where UVR-  
20 6128 is used in place of the more rigid UVR 6110 molecule  
(Formulations 2C and 2E).

Stability data, as measured by modulus change after conditioning  
at 95°C/95% RH for 20 and 30 days are given in Table 1 and after 6  
days in Table 2. For the purposes of the present invention, the modulus  
25 should not change by more than about 20% after 30 days at 85°C/85%  
RH. The precision of the modulus measurement is approximately  
+/-5%. Therefore, the precision of the modulus change measurement  
will be greater than 5%. The data presented in the tables indicate good  
retention of modulus for vinyl ether formulation 1A. At 20 days the vinyl  
30 ether formulations with approximately 20% acrylate monomer are  
reasonably stable as is the vinyl ether formulation 1B based on the vinyl  
ether urethane oligomer. However, at 30 days all these latter materials  
have markedly increased in modulus. The use of the Vectomer 2032 type  
oligomer may, therefore, be limited by stability requirements in the  
35 particular application of the system. Nonetheless, the basic and  
underlying concept of the present invention has been shown.

-19-

This is also a practical limitation in the amount of acrylate monomer that can be added while maintaining adequate temperature and humidity stability for many applications. Chemical kinetics would suggest that all of the above formulations would have been acceptable after 30 days at 85°C/85% RH. Moreover, the color stability of the vinyl ether compounds based on the ester type oligomer (Formulations 1A, 1F, 1G and 1H) was good, showing only a slight off color tint after the 30 day test. Matrix compound 1B was significantly off color and would not be acceptable without further stabilization in applications where color stability is an important criteria.

A matrix compound (formula 2A) based on cycloaliphatic epoxides and polyols showed poor performance in the 95°C/95% RH test indicating that this type compound is limited to applications where high temperature, high humidity stability is not critical.

Specific formulations for the inks tested are given in Table 3. As used in that Table, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 is a free radical-type photoinitiator which is sold under the trade name Irgacure 907 (Ciba-Geigy Corp., Hawthorne, NY). TiO<sub>2</sub> is a white pigment available from multiple sources, *e.g.*, Tronox CR-800 from Kerr-McGee Chemical Corp. Bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate is a hindered amine light stabilizer sold under the trade name Tinuvin 770 (Ciba-Geigy Corp., Hawthorne, NY). The other blend components listed in Table 3 have been previously described.

-20-

**TABLE 3**  
**UV INK FORMULATIONS:**

COMPONENTS:	INK IDENTIFICATION (PARTS BY WEIGHT)				
	UV1	UV2	UV3	UV4	UV5
EBECRYL 8804	68.25	68.25	68.25	68.25	68.25
TMPTA	18.9	18.9	18.9	18.9	18.9
HDODA	10.5	10.5	10.5	10.5	10.5
TRPGDA	7.35	7.35	7.35	7.35	7.35
TiO <sub>2</sub>	5.0	5.0	5.0	5.0	5.0
IRGANOX 1076	1.0	1.0	1.0	1.0	1.0
IRGACURE 907	3.0	--	1.5	0.75	--
IRGACURE 651	--	3	1.5	2.25	3.0
SF-1188	0.5	0.5	0.5	0.5	0.5
TINUVIN 770	--	--	--	--	1.0

- 5           Test plaques for determination of T-peel Adhesion were prepared as follows. An approximate 75 micron thickness of Desolite® Product Code 950-044 optical fiber coating (DSM Desotech Inc., Elgin, IL), an industry-known UV curable acrylate coating, having a viscosity of 5000 cps at 25°C and a tensile modulus upon curing of 690 MPa at 23°C, 50% relative humidity, is cured at a cure dose of 500 mj/cm<sup>2</sup> using a Fusion Systems D bulb under a nitrogen blanket. The cured film is held for at least one day before proceeding to the next step. After the holding period, an approximate 10 micron thickness layer of a UV curable acrylate polymer based ink is then applied and cured under a nitrogen blanket with a Fusion Systems H bulb at a cure dose of 250 mj/cm<sup>2</sup> (this step is skipped for non-color coded testing). The color coded composite is then held for at least one day before proceeding. In the final step, an approximately 75 micron thick layer of matrix compound is applied at a
- 10
- 15

-21-

temperature of 60°C and then cured with a Fusion Systems H bulb at a cure dose of 500 mj/cm<sup>2</sup> under a nitrogen blanket. In some tests, a release layer is applied to the top of the composite to provide a non-bonded layer at the top of the test composite. The finished composite is again held for at least 48 hours. Tape (Scotch® 3M mailing tape, 3M, Minneapolis, MN) is then applied to both sides of the sample for support to prevent tensile failure of the composite, a 1 inch wide test strip is cut, and a separation made by hand at the interface between the ink and the matrix compound in the non-bonded region. A T-peel test is then run on a Thwing-Albert tensile tester at a crosshead rate of 2 in./min. The peel level is recorded along with the failure interface.

Test data for the various matrix compound and ink combinations are given in Table 4. As can be seen, formulations 1A and 1B (which contain no acrylate components) have very low adhesion to the optic fiber coating material when no ink is present. When the UV1 or UV2 ink is applied, adhesion of 1A (which contains a vinyl ether encapped urethane oligomer) remains low. However, adhesion of 1B (which contains a vinyl ether encapped oligomer) remains low. However, adhesion of 1B (which contains a vinyl ether encapped ester oligomer) increases significantly.

-22-

TABLE 4  
MATRIX ADHESION  
(T-PEEL ADHESION, pounds/inch width)

FIBER COATING		D950-044 BASE						1A	
INK ID		NONE	UV1	UV2	UV3	UV4	UV5	NONE	UV2
% MATRIX ACRYLATE ID: IN MATRIX									
1A	0	0.01	0.02, 0.04	0.10, 0.11	0.01	0.03			
1B	0	0.02	0.55	0.57					
1N	0	0.01	0.02	0.09			0.04		
1L	100 <sup>d</sup>		>2.04	>1.42				0.02	0.02
1E	10 <sup>a</sup>		0.06	0.09					
1H	20 <sup>a</sup>		0.22	0.15					
1K	50 <sup>a</sup>		>3.15	0.70					
1C	10 <sup>b</sup>		0.13	0.10					
1F	20 <sup>b</sup>		0.10	0.20					
1I	50 <sup>b</sup>		>1.86	>1.83					
1D	10 <sup>c</sup>		0.06	0.10					
1G	20 <sup>c</sup>		0.07	0.09					
1J	50 <sup>c</sup>		0.25	0.40					
1M	50 <sup>d</sup>		0.5	>2.19					
2A	0	0.04	0.14	>1.42					
2B	10 <sup>a</sup>		>1.72	>1.48					
2C	0		0.34 <sup>f</sup>						
2D	0		0.66 <sup>f</sup>						
2E	0		>1.51 <sup>f</sup>						
2F	0		0.07 <sup>f</sup>						

a: TRPGDA

b: HDODA

c: TMPTA

d: MONOMER + OLIGOMER

e: Matrix layer cured at 40°C

f: Matrix layer cured at ambient

UV1 and UV2 both contain an urethane acrylate oligomer.

Therefore, the inks in those cases contain an oligomer which is more chemically similar to the 1B matrix compound than the 1A matrix compound. Hence, the adhesion of 1B to the ink is greater than 1A to the ink.

As various acrylate components are added to the 1A type matrix (matrix materials 1C through 1M), the adhesion can be increased to obtain a desired level. The greater the acrylate content of the matrix, the greater the chemical similarity between the matrix and the ink and, therefore, the greater the adhesion. Once the matrix acrylate content has reached about 50%, the adhesion is too high to obtain a meaningful test. Where the greater than (>) sign is shown in Table 4, the peel occurs between the back-up tape and the matrix compound indicating that the peel adhesion level between the ink and the matrix compound is at a higher level than can be determined by this test configuration. In all other test samples, the peel interface is between the ink and the matrix compound or between the matrix compound and fiber coating material where no ink is present.

It is apparent from the above-data that combinations of vinyl ether encapped urethane and ester oligomers can also be used to control the peel adhesion.

Additionally, the data shows that if the ink is based on a ester acrylate oligomer, that the matrix compound 1B above would have lower peel adhesion to the ink than would matrix compound 1A.

Moreover, in a mixed acrylate/vinyl ether or other cationic cure system, both cationic and free radical type UV activated initiators are required.

To determine the viability of embodiments where the ink contains an inhibitor of the cationic cure matrix materials, four different blends of ink were prepared by adding 1.0 percent by weight of four components to formulation 1A in Table 1. These materials were Irgacure 651, Irgacure 907 (previously described as an initiator for acrylate systems), 1-vinyl-2-pyrrolidone (NVP), and a hindered amine light stabilizer bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate which is sold under the trade name Tinuvin 770 (Ciba-Geigy Corp., Hawthorne, NY). The materials were cured as previously described for matrix compounds. In these tests, the blends containing Tinuvin 770 and Irgacure 907 did not cure but remained



-24-

viscous liquids even after exposure to UV light. The blend containing NVP, upon exposure to UV light, yielded a uncured, tacky film which was too fragile for tensile analysis. The blend containing Irgacure 651 was well-cured.

5           The viability of cure inhibition in a free-radical based polymer matrix was tested by the addition of 0.5% and 0.25% by weight of naphthaquinone to the acrylate coating Desotech® 950-44. A similar amount was added in the reverse case for matrix 1N. On exposure to a 500 mj/cm<sup>2</sup> dose of UV radiation, the 950-044 with 0.5% naphthaquinone  
10           produced a low modulus, greatly uncured product. The 1N matrix was slightly uncured. At a 0.25% naphthaquinone level, the 950-044 again was uncured with a modulus of 18 MPa. The 1N matrix with 0.25% naphthaquinone was well-cured with a modulus of 418 MPa.

          Table 4 sets forth peel adhesion data for Matrix 1A from inks  
15           containing 3 parts by weight of Irgacure 907 (UV1) and Irgacure 651 (UV2). As can be seen, there is a decrease in adhesion when going from the Irgacure 651 to the Irgacure 907 containing ink. Examination of the molecular structure of Irgacure 907 shows it to be a hindered amine. UV3 and UV4 inks have a combination of Irgacure 651 and Irgacure 907  
20           initiators. In combination with matrix 1A, both of these inks also show lower adhesion relative to UV2 and Matrix 1A. When the hindered amine light stabilizer Tinuvin 770 is added to the ink (UV5) and Matrix 1N is used, a similar drop in peel adhesion is seen relative to the UV2/1N combination.

25           Table 4 also describes peel adhesion data for cationic cure systems based on cycloaliphatic epoxide/polyol combinations. As can be seen from tests conducted with Matrix materials 2A through 2E, values are somewhat higher than those obtained using formulations based on vinyl ether chemistry. In fact, it appears necessary to use Irgacure 907 in the  
30           ink to properly reduce the peel adhesion. Furthermore, use of the trifunctional polyol 0301 results in lower adhesion than does polyol 0201. Increasing the level of 0201 also increases the adhesion. When

-25-

combinations of the two chemistries are used as in formula 2F, the adhesion reading falls between the values reported for the non-mixed formulations. These data support the finding, based upon the present disclosure, one of skill in the art could formulate the various components to obtain a desired adhesion level without undue experimentation. Other properties, such as modulus and stability, will dictate which combinations are most desirable in obtaining the final properties depending upon the desired application.

Based upon the disclosure of the present invention, if the optical fiber coating is a cationic material, it would be desirable to use a cationic cure ink for adhesion to the fiber coating and an acrylate based matrix for release from the cationic ink. Table 4 also demonstrates that this is the case. For example, when Matrix 1A was cured first, *i.e.*, as the optical fiber coating, subsequent cure of the acrylate ink UV2 or acrylate matrix 1L on the vinyl ether coating surface resulted in poor adhesion. Hence the ink used where the fiber coating is substantially a cationic cure compound should also be comprised substantially of a cationic cure components and the matrix compounds should be comprised substantially of free radical initiated acrylate type components.

-26-

What is claimed is:

1. A removable matrix for retaining on or more optical fibers having an outermost layer comprising a first polymer with a first initiator system, the matrix comprising a second polymer having a second initiator system substantially different from the first initiator system.

2. The matrix of Claim 1, wherein the first and second polymers are radiation curable polymers.

3. The matrix of Claim 1, wherein the first polymer comprises a free radical initiated, ultraviolet radiation curable polymer and the second polymer comprises a cationically initiated, ultraviolet radiation curable polymer.

4. The matrix of Claim 3, wherein the free radical initiated, ultraviolet radiation curable polymer is an acrylate polymer.

5. The matrix of Claim 4, wherein the matrix further comprises a partial adhesion promoting amount of a free-radical initiated, radiation curable acrylate polymer and wherein the cationically initiated, ultraviolet radiation curable polymer comprises a major portion of the matrix and the free-radical initiated, ultraviolet radiation curable acrylate polymer comprises a minor portion of the matrix, whereby the presence of the free-radical initiated, ultraviolet radiation curable acrylate polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

6. The matrix of Claim 3, wherein the cationically initiated, ultraviolet radiation curable polymer comprises a mixture of cycloaliphatic epoxide and a polyol.

7. The matrix of Claim 3, wherein the cationically initiated, ultraviolet radiation curable polymer comprises a vinyl ether polymer.

8. The matrix of Claim 7, wherein the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer, a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof.

-27-

9. The matrix of Claim 8, wherein the vinyl ether encapped ester oligomer is Allied Signal 150B.

10. The matrix of Claim 8, wherein the vinyl ether encapped urethane oligomer is Vectomer 2032.

11. The matrix of Claim 8, wherein the vinyl ether encapped monomer is bis-(4-vinyloxybutyl) isophthalate.

12. The matrix of Claim 8, wherein the vinyl ether encapped monomer is 4-vinyloxybutyl benzoate.

13. The matrix of Claim 1, wherein the first polymer comprises a cationically initiated, ultraviolet radiation curable polymer and the second polymer comprises a free radical initiated, ultraviolet radiation curable polymer.

14. The matrix of Claim 13, wherein the free radical initiated, ultraviolet radiation curable polymer is an acrylate polymer.

15. The matrix of Claim 13, wherein the matrix further comprises a partial adhesion promoting amount of a cationically initiated, ultraviolet radiation curable polymer and wherein the free-radical initiated, ultraviolet radiation curable polymer comprises a major portion of the matrix and the cationically initiated, ultraviolet radiation curable polymer comprises a minor portion of the matrix, whereby the presence of the cationically initiated, ultraviolet radiation curable polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

16. An optical fiber and matrix ribbon, the ribbon comprising:

- a) one or more optical fibers, wherein the fibers have an outermost layer comprising a free-radical initiated, ultraviolet radiation curable acrylate polymer; and
- b) a removable matrix for retaining the one or more optical fibers, wherein the matrix comprises a cationically initiated, ultraviolet radiation curable polymer.

17. The ribbon of Claim 16, wherein the matrix further comprises a free-radical initiated, radiation curable acrylate polymer and wherein the cationically initiated, ultraviolet radiation curable polymer comprises a major portion of the matrix and the free-radical initiated, ultraviolet radiation curable acrylate polymer comprises a minor portion of the matrix, whereby the presence of the free-radical initiated, ultraviolet radiation curable acrylate polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

18. The ribbon of Claim 16, wherein the cationically initiated, ultraviolet radiation curable polymer comprises a vinyl ether polymer.

19. The ribbon of Claim 18, wherein the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer, a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof.

20. The ribbon of Claim 19, wherein the vinyl ether encapped polymer is Allied Signal 150B.

21. The ribbon of Claim 19, wherein the vinyl ether encapped urethane oligomer is Vectomer 2032.

22. The ribbon of Claim 19, wherein the vinyl ether encapped monomer is bis-(4-vinyloxybutyl) isophthalate.

23. The ribbon of Claim 19, wherein the vinyl ether encapped monomer is 4-vinyloxybutyl benzoate.

24. The ribbon of Claim 16, wherein the outermost layer of the one or more fibers comprises an ink coating, wherein the ink comprises a free-radical initiated, radiation curable acrylate polymer.

25. The ribbon of Claim 24, wherein the ink further comprises an inhibitor of cationically initiated polymerization.

26. The ribbon Claim 25, wherein the inhibitor is water, a basic compound, or a mixture thereof.

27. The ribbon of Claim 25, wherein the inhibitor is a pigment capable of interacting with the cation.

28. The ribbon of Claim 25, wherein the inhibitor is a hindered amine light stabilizer.

29. The ribbon of Claim 28, wherein the hindered amine light stabilizer is bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate.

30. The ribbon of Claim 25, wherein the inhibitor is 1-vinyl-2-pyrrolidone.

31. An optical fiber and matrix ribbon, the ribbon comprising:

- a) one or more optical fibers, wherein the fibers have an outermost layer comprising a cationically initiated, ultraviolet radiation curable polymer; and
- b) a removable matrix for retaining the one or more optical fibers, wherein the matrix comprises a free-radical initiated, ultraviolet radiation curable acrylate polymer.

32. The ribbon of Claim 31, wherein the matrix further comprises a cationically initiated, ultraviolet radiation curable polymer and wherein the free-radical initiated, ultraviolet radiation curable acrylate polymer comprises the major portion of the matrix and the cationically initiated, ultraviolet radiation curable polymer comprises the minor portion of the matrix, whereby the presence of the cationically initiated, ultraviolet radiation curable polymer promotes partial adhesion between the outermost layer of the one or more fibers and the matrix.

33. The ribbon of Claim 31, wherein the cationically initiated, ultraviolet radiation curable polymer comprises a vinyl ether polymer.

34. The ribbon of Claim 31, wherein the outermost layer of the one or more fibers comprises an ink coating, wherein the ink comprises a cationically initiated, ultraviolet radiation curable polymer.

35. The ribbon of Claim 34, wherein the ink further comprises an inhibitor of free-radical initiated polymerization.

36. The ribbon of Claim 35, wherein the inhibitor comprises a benzoquinone derivative.

37. The ribbon of Claim 35, wherein the inhibitor comprises hydroquinone, naphthaquinone, or a mixture thereof.

38. An ink for use on an acrylate polymer coated optical fiber, wherein the ink comprises an inhibitor of cationically initiated polymerization.

39. The ink of Claim 38, wherein the inhibitor is water, a basic compound, or a mixture thereof.

40. The ink of Claim 38, wherein the inhibitor is a pigment capable of interacting with the cation.

41. The ink of Claim 38, wherein the basic compound comprises a hindered amine light stabilizer.

42. The ink of Claim 41, wherein the hindered amine light stabilizer is bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate.

43. The ink of Claim 38, wherein the inhibitor is 1-vinyl-2-pyrrolidone.

44. The ink of Claim 38, wherein the inhibitor is an initiator of free radical initiated polymerization.

45. The ink of Claim 44, wherein the inhibitor is 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1.

46. A matrix comprised of a cationically initiated, ultraviolet radiation curable vinyl ether polymer.

47. The matrix of Claim 46, wherein the vinyl ether polymer is a vinyl ether encapped ester oligomer, a vinyl ether encapped urethane oligomer, a vinyl ether encapped ester monomer, a vinyl ether encapped alcohol, or a mixture thereof.

48. The matrix of Claim 46, wherein the vinyl ether encapped ester oligomer is Allied Signal 150B.

49. The matrix of Claim 46, wherein the vinyl ether encapped urethane oligomer is Vectomer 2032.

50. The matrix of Claim 46, wherein the vinyl ether encapped monomer is bis-(4-vinyloxybutyl) isophthalate.

51. The matrix of Claim 46, wherein the vinyl encapped monomer is 4-vinyloxybutyl benzoate.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/17800

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G02B6/44

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 533 397 (AMERICAN TELEPHONE & TELEGRAPH) 24 March 1993 see claims 1-10 see page 3, line 22 - line 44 see page 4, line 3 - page 6, line 33 see page 7, line 1 - line 6; figure 6 ---	1
A	EP,A,0 407 004 (BORDEN INC) 9 January 1991 see claims 1-26,40-43,45,57 see page 5, line 41 - page 6, line 6 see page 7, line 3 - line 45 ---	1
A	EP,A,0 262 340 (SUMITOMO ELECTRIC INDUSTRIES) 6 April 1988 cited in the application see claim 1 see page 4, line 26 - page 5, line 5 see page 5, line 33 - page 6, line 12 ---	1
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

21 January 1997

Date of mailing of the international search report

29.01.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Depijper, R



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/17800

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 349 206 (AMERICAN TELEPHONE & TELEGRAPH) 3 January 1990 see claims 1-10 see page 5, column 7, line 50 - column 8, line 34 see page 6, column 10, line 18 - line 48 ---	1
A	WO,A,89 03761 (LOCTITE CORP) 5 May 1989 see claims 1-4,6-8 see page 7, paragraph 2 see page 11, paragraph 4 - page 15, paragraph 2 see page 15, paragraph 3 - page 17 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/17800

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0533397	24-03-93	US-A- 5181269	19-01-93
		AU-B- 654209	27-10-94
		AU-A- 2456192	18-03-93
		CA-A, C 2074909	18-03-93
		CN-A- 1070738	07-04-93
		JP-A- 6250053	09-09-94
-----			
EP-A-0407004	09-01-91	AT-T- 141301	15-08-96
		AU-B- 622752	16-04-92
		AU-A- 4853290	10-01-91
		DE-D- 69028051	19-09-96
		DE-T- 69028051	02-01-97
		ES-T- 2090096	16-10-96
		JP-A- 3039314	20-02-91
-----			
EP-A-0262340	06-04-88	AU-A- 7653687	11-02-88
		CA-A- 1301509	26-05-92
		DE-D- 3751584	14-12-95
		DE-T- 3751584	21-03-96
		US-A- 4828349	09-05-89
-----			
EP-A-0349206	03-01-90	US-A- 4900126	13-02-90
		CA-A- 1331530	23-08-94
		CN-A- 1039121	24-01-90
		JP-A- 2047606	16-02-90
-----			
WO-A-8903761	05-05-89	US-A- 4892764	09-01-90
		AT-T- 126478	15-09-95
		AU-A- 2909789	23-05-89
		CA-A- 1335494	09-05-95
		DE-D- 3854330	21-09-95
		DE-T- 3854330	14-03-96
		EP-A- 0380591	08-08-90
		IL-A- 88032	28-11-94
		JP-B- 7113065	06-12-95
		JP-T- 3500665	14-02-91
		US-A- 5305601	26-04-94
-----			